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Preparation and Spectroscopic Characterization of Chromium(III) and Iron(III) Mixed Ligand Complexes

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Abstract .Curcumin (Cur) and L phenylalanine (Phy) compounds were used to prepare two mixed ligand complexes with Cr (III) and Fe (III) ions. The synthesized complexes are characterized by using conductivity measurement and different spectral methods like FT-IR and UV- Vis .Molar conductance and analytical studies confirmed that the complexes exhibit octahedral geometry., suggest that the complexes are formed in 1: 1 :2 [L : Metal : 2phe] ratio and they proposed to have the general formulae $[M(\text{Cur})(\text{phe})_2] \text{Cl}$ (M= Cr (III) and Fe (III)) The compound dyeing method was studied and applied to acrylic fabric.The antibacterial activity of curcumin, phenylalanine and their mixed ligand complexes were examined on pathogenic bacterial strains and showed good results ,

Keywords: L-Phenyl alanine , Biological Activities And Curcumin

Introduction

Curcumin; 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione is a component of the Indian spice turmeric, synthesized from the rhizome of the perennial herb *Curcuma longa* that is widely cultivated in tropical countries in South and South East Asia, especially in India and China. Curcumin is the major component of three curcuminoids that give turmeric its characteristic yellow color and is used as a food colorant and flavoring[1]. Metal-organic compounds have a great importance in different areas such as; analytical, catalytic, biological and cell devisions,e.t.c. This is refer to the selective of oxidation state of the used metal ions in the coordination sphere or due to their unused chelation sites exist on metal and ligand systems[2]. Subhan et. al.[3] Prepared and characterized six metal complexes with curcumin ligand by using CHN elemental analyses and spectral techniques[IR and electronic]. The IR spectral data showed that the ligand behaves a bidentate form. Also the antibacterial activity of the ligand and its complexes were tested against several pathogenic bacteria and it is found that Cr(III) complex displayed a better effect against *Klebsiella* , *E. Coli* and *Psydomonus* than other metal-curcumin complexes. Meanwhile, Pd(II) and Y(III) also exhibited a little activity against all testing bacteria. A series of copper(II) complexes of curcumin compound have been synthesized and characterized by physiochemical tools, such as; elemental analysis, molar conductivity, magnetic moment measurements, infrared, electronic, NMR and electrochemical studies. Also the antioxidant and the binding behavior of the complexes with DNA have been investigated.[4]



The present paper deals with the Preparation, magneto chemical and spectral studies of mixed ligand Complexes of [Cr (III) and Fe(III)]ions using (Curcumin)as a primary ligand and (L-phenylalanine) as a secondary ligand.

Experimental

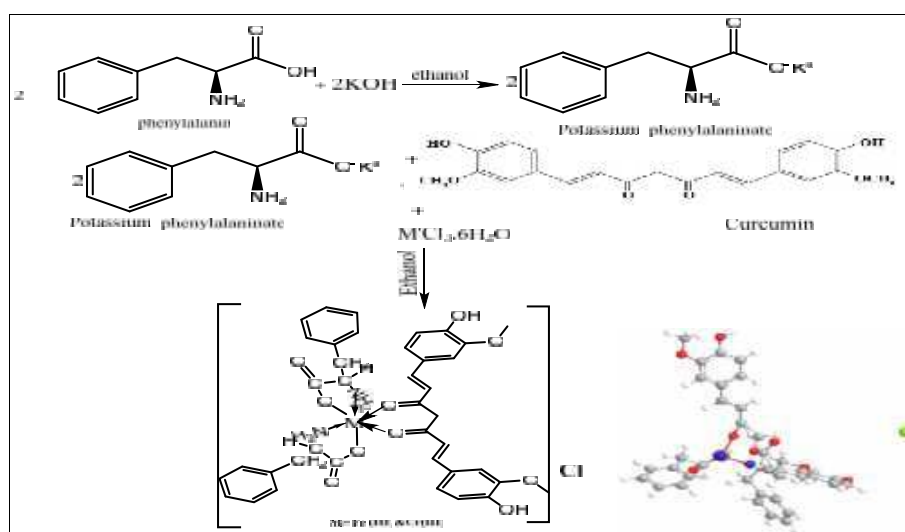
Chemicals and Methods

All chemicals used in this study are of Aldrich or BDH quality including Curcumine , L-phenylalanine, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, ethanol, KOH, DMSO,. IFS-25DPUSR-IR spectrometer (Bruker) was used to record the IR spectra of the mixed ligand complexes in the range of $4000\text{-}40\text{cm}^{-1}$. Perkin-Elmer-Lambda spectrophotometer was used to illustrate the electronic spectra of the complexes in DMSO solvent. Magnetic susceptibility measurements were carried out by using " Bruker magnet BM6 device " at 298°K .

Synthesis of $[\text{M}(\text{CUM})(\text{Phe})_2]\text{Cl}$ complexes

L- phenylalanine [0.33 gm, 2m mol] was dissolved in 20 mL ethanol and added to 10 mL of ethanolic solution containing [0.112 gm (2mmol)] of the potassium hydroxide (KOH), in a flask and stirred at room temperature (27°C). The solution was deprotonated according to the scheme (1)

The resulting complexes were washed several times with hot ethanol until the filtrate becomes clear, dried in air. The yield ranged from 70-85%. The all obtained complexes are soluble in DMSO solvent. The melting points of the prepared mixed ligand complexes were measured and found to be $>250^\circ\text{C}$. The dried complexes were subjected to spectroscopic analyses. [5]



Scheme (1) Representation of Preparation the complexes Dyeing methods

Yarn fibers of (wool and cotton) threads of goat were used for each dyeing experiment. The wool and cotton were obtained from the dye stuff was extracted with boiling water by applying a bath liquor ratio of (g/ml). The duration of the extraction was fixed at one hours. Yarn samples were dyeing without Mordant placed in a glass beaker of one liter capacity containing 500 mL of dyestuff and boiled for 50 minutes. The yarn samples were rinsed with distilled water and air dried. [6-7]

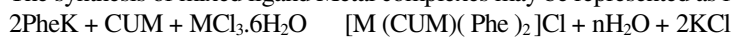
Antibacterial assay

Two types of human pathogenic bacteria [*Staphylococcus aureus* and *Escherichia coli*] and *Candida albicans* fungal strains were used to test the biological effects of the present mixed ligand complexes. The two

species of bacteria were streaked on nutrient agar (OXID England) plates, so that the streaking covered the surface of the plates. The plates were incubated at [37 °C for 24 hrs]. The inhibition zones were then measured in millimeters and recorded.

Results and discussion

The synthesis of mixed ligand Metal complexes may be represented as follows:

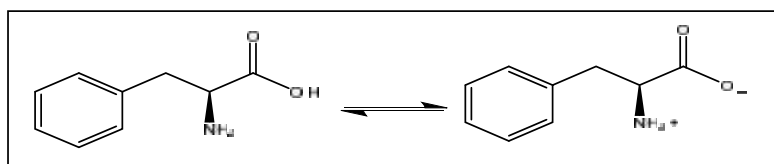


{where (CUM) is Curcumin and (Phe) is amino acid L-phenylalanine

M = Cr(III) & Fe(III)}. The suggested (molecular formula), color, Molecular Weight, melting points, temperatures, M% and conductivity of the complexes are given in Table (1) for all new complexes. Curcumin (CUM) is poorly soluble in (H₂O) and solubilized in (C₂H₅OH) and dimethyl sulfoxide (DMSO). The obtained molar conductance values Table-1 reveal the existence of electrolytic nature for Cr(III) and Fe(III) complexes. [5]

The metal contents% of the mixed ligand metal complexes were carried out by the direct method using AAS analysis. [6] The theoretical and experimental values of metal percentage in each complex are in fair agreement. These results are very supportive of the proposed formulae of the complexes.

In order to determine the coordination sites of the curcumin and L-phenylalanine ligands toward the used metal ions, IR spectra of the complexes were recorded to confirm their structure. The assignment of the characteristic bands of the free ligands and their mixed ligand complexes are listed in tables 2, 3, and 4. The chelation of amino acid such L-phenylalanine was evidently present in its (zwitterion form) and, therefore, the N-H moiety must be protonated, generating a (NH₃⁺) group, whereas, the acid group remains in the anionic (COO⁻) form, Scheme-1 and the IR spectra of these cannot be compared entirely with those of complexes as amino acids in metal complexes which do not exist as zwitterions. [7-8]



Scheme (2) Zwitterions of L-Phenylalanine

The IR spectrum of (Phy) exhibits a band at 3410 cm⁻¹ corresponds to ν (N-H) + ν (O-H), while, another strong absorption band at 3350 cm⁻¹ is due to the ν (NH₂), meanwhile, the bands at 1662 and 1485 cm⁻¹ were assigned to the ν (-COO⁻) asym and ν (-COO⁻) sym respectively. [9]

The spectrum of (CUM) shows strong broad band in the range of 3059 -3475 cm⁻¹ which assigned to hydrogen bonded (OH) phenolic and strong band at 1627 cm⁻¹ which is assigned to (C=O). Moreover, coordination of the (C=O) group to the metal ion is suggested by the shift to the (C=O) band. The bands at 1157, 1438, 3066 cm⁻¹ due to (C-O-C), (Ar-C=C) and (Ar C-H), respectively. [10]. The infrared spectra of the prepared mixed ligand complexes were recorded by using KBr disk in the range 400-4000 cm⁻¹, the important group frequencies of the (-COO)_{asy},

(-COO)_{sym}, (N-H₂), (C=O), (C=C, CH) aromatic and (O-H) stretching vibrations. In conclusion, our investigation suggests that the ligands (CUM) and (L-Phy), their peaks at 3502, 1627, 1601, (1505, 1427, 1358) and 1272 cm⁻¹ are due to the (Ph-OH) and carboxyl group (COO⁻), (C=C), (Ar C=C) (3peaks), (C-O) and two bands at 1635 and 1573 cm⁻¹ were assigned to stretching C=O vibration. On the complexation, these bands have been shifted to higher frequency in the spectra of all complexes. [11] Absorption bands in the range of 520-597 cm⁻¹ are considered to be due to metal-nitrogen (M-N) vibrations, [12] whilst, those occurring around 412-470 cm⁻¹ are thought to arise from metal-oxygen (M-O) vibration. [13] The results showed that the deprotonated of L-phenylalaninate interacts with all of these two metal ions as a mono negative bidentate fashion through oxygen of the carboxylic group and nitrogen of the amine group to M (III) ions, while, curcumin (Cur) coordinates as neutral bidentate through (O) in (C=O) group. The energy difference between both vibrations [asym (COO⁻)] [sym (COO⁻)] > 200 cm⁻¹, from IR spectral data that's supports the collaboration of this group in monodentate binding.

Electronic spectra of the ligands and their complexes

The UV spectrum of (Phe), exhibits two peaks at 272 nm (36764 cm^{-1}) and 330 nm (30303 cm^{-1}) which are appointed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, [14] Whereas, the UV absorption of curcumin(cur), fig.6 shows two absorption peaks at around 430 nm (23255 cm^{-1}) and 265 nm (37735 cm^{-1}) can be due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions,

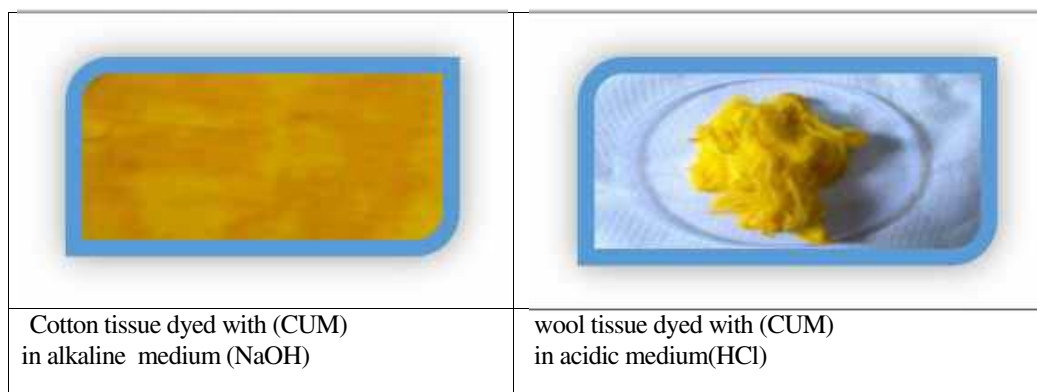
respectively, in the aromatic ring agree with data reported by several research workers.[15] The maximum absorption is due to the electronic dipole allowed $\pi \rightarrow \pi^*$ type excitation of its extended conjugation system and polar chromophores in curcumin molecule, this solvent tends to stabilize both the bonding electronic ground states and the $\pi \rightarrow \pi^*$ excited states. The magnetic moment value of $[\text{Cr}(\text{cur})(\text{Phe})_2]\text{Cl}$ is 3.66 B.M analogous to the presence of three unpaired electrons close to spin only value, that a tentative interpretation expects the structure of Cr (III) to be an octahedral geometry [16], the first and second have high intense peaks at 265 nm (37735 cm^{-1}) and 309 nm (32362 cm^{-1}) are due to the ligand field and intra-ligand charge transfer (INCT) respectively, and shows other three bands at 430 nm (23255 cm^{-1}), 681 nm (14684 cm^{-1}) and 974 nm (10266 cm^{-1}) (Table 3) which are assignable to $(4A_2g(F) \rightarrow 4T_1g(F))$ (3), $4A_2g(F) \rightarrow 4T_1g(F)$ (2) and $(4A_2g(F) \rightarrow 4T_2g(F))$ (1), respectively. [17]. $\nu = \{1/\lambda(\text{nm})\} (1 \times 10000000) \text{ cm}^{-1}$

$\nu = E = 10266 \text{ cm}^{-1} = 10 \text{ Dq}$. We can using the other energy units
 $1 \text{ cm}^{-1} = 1.24 \times 10^{-4} \text{ eV} = 0.01196 \text{ kJ/mol}$, $E = \nu = 10266 \times 1.24 \times 10^{-4} = 1.27 \text{ eV}$, $E = \nu = 10266 \times 0.01196 = 122.78 \text{ kJ/mol}$. The spectral parameters of the Cr(III) complex are as follows [15-17]: ν_1/ν_2 ratio is 0.69, $\text{Dq} = 10266 \text{ cm}^{-1}$, The ν_2/ν_1 ratio is 1.43, which is in the usual range reported for an octahedral Cr(III) complexes

The μ_{eff} value for $[\text{Fe}(\text{CUM})(\text{Phe})_2]\text{Cl}$ complex is 6.06 B.M., that a tentative interpretation expects the structure of Fe(III) to be an octahedral geometry agree with data reported by several research workers [18]. The (U.V- Vis) spectrum, Figure (3-19) exhibits four transitions. The first and second high intense peak at 270 nm (37037 cm^{-1}) and 432 nm (23148 cm^{-1}) are due to the ligand field and intra ligand charge transfer (INCT) respectively and show other two bands at 745 nm (13422 cm^{-1}), 820 nm (12195 cm^{-1}), which are assignable to ${}^6A_1g(S) \rightarrow {}^4T_1g$ (3) and ${}^6A_1g(S) \rightarrow {}^4T_2g$ (2) respectively.

Dyeing Performance

The dyeing method of the compounds were studied and applied on wool and cotton. These set dyes were given colors as shows in figure (1) The role of the metal atom is to form a complex with the dyestuff already present on the fabric. The obtained results in dyeing with the all complexes are summarized in Tables 4,5 show the effects on cotton and wool samples. The dye molecules are typically a diketone structure which can contain additional groups like hydroxyl, carbonyl or amino groups. They can form strong coordination complexes with, chromium and Iron ions due to which free amino group are protonated, which cannot then form coordinate bonds with the metal atom, as a result coordination between amino group of the protein and ions of the dye is suppressed. The obtained results in dyeing with the all complexes is summarized in Table (6), shows the effects on Cotton and wool samples.



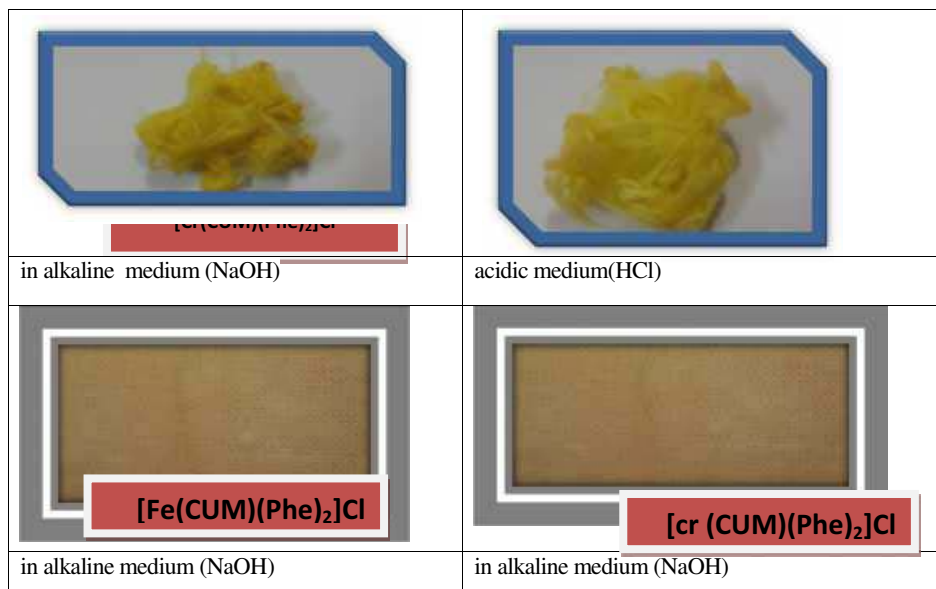


Figure (1) Samples of wool and cotton tissues dyeing by metal complexes in acidic (HCl) and alkaline (NaOH)

Table (1) Some physical properties of the compounds

Chemical Formula	Color	M.wt	m.p °c	M% Γtheor.) Exp.	(Λ _M) 1000L/C Ω ² m ² mol ⁻¹ (DMSO)	Elect. Nature
[Cr(CUM)(Phe) ₂]Cl	Dark yellow	786.26	250	(5.09) 6.61	47.18	1:1 elect
[Fe(CUM)(Phe) ₂]Cl	Dark brown	790.1	215	(5.7) 7.06	40.1	1:1 elect

Table (2) Assignment of infrared frequencies in Cm-1of the (L-Phe)

ν (N-H) + ν (O-H)	ν(NH ₂) sy	ν(C-H) aliphatic	ν(C= C)	COO ⁻)asy(ν 1662s	COO ⁻)sy(ν 1485s	COO ⁻ asy - COO ⁻ sy)(177
3410 3350	3095	2962	1496			

Table(3) Infrared spectrum data (wave number ó) cm-1 for the (CUM)

phenolic ν(OH)	ν(C-H) aromatic	ν ν ν (δ ν (C (-OCH ₃) al
3444	3066	2911 1611 1157 1133

Table(4) FT-IR spectra data (wave number ν) cm^{-1} for the mixed -ligand (CUM –M-Phe) complexes.

Complexes	ph (C-H) aromatic	(C=C) aromatic	(C=C) aliphatic	(C=C) aliphatic	(N-M)
[Cr(CUM)(Phe) ₂]Cl	3433, 3086	3086	2916, 1412, 2255, 4513	2916, 1412, 2255, 4513	5641
[Fe(CUM)(Phe) ₂]Cl	3430, 3059	3059	2916, 1412, 2913, 5641	2916, 1412, 2913, 5641	5641

Table (5) Electronic spectral data of (CUM - M-phe) complexes

Comp.	nm	ν cm^{-1}	max $\text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$	Assignments	μ_{eff} <i>B.M</i>
[Cr(CUM)(Phe) ₂]Cl	265	37735	218		3.66
	309	32362	108	charge transfer	
	430	23255	452	${}^4\text{T}_{1g}(\text{P})$ 3	
	681	14684	13	${}^4\text{T}_{1g}$ 2	
[Fe(CUM)(Phe) ₂]Cl	974	10266	18	${}^4\text{A}_{2g}$ ${}^4\text{T}_{2g}$ 1	6.01
	270	37037	140.4	L.F	
	432	23148	775	charge transfer	
	745	13422	30	${}^5\text{A}_{1g}(\text{S})$ ${}^4\text{T}_{1g}$ (3) ${}^6\text{A}_{1g}(\text{S})$ ${}^4\text{T}_{2g}$ (
	820	12195	27		

Table (6) Shows the effects dyeing by metal complexes on wool and cotton

Chemical Formula	Color cotton dyeing in the alkaline medium (NaOH) (Color wool dyeing in the acidic medium (HCl)
[Cr(CUM)(Phe) ₂]Cl	Brown	Yellow
[Fe(CUM)(Phe) ₂]Cl	Brown	Yellow

Biological activity

All the compounds including DMSO (as solvent and control). The Zones of inhibition (IZ) based upon zone size around the discs were measured [20]. The bacterial culture for the bacteria namely, *Staphylococcus aureus* and *Escherichia coli* was grown on nutrient agar medium. From the result obtained, it has been found that the tested complexes show a little activity against *Staphylococcus aureus* and *Escherichia coli* [Figure 2]. The antifungal activity results indicated that

[Cr (Cum)(Phe)₂]Cl and [Fe (Cum) (Phe)₂] Cl Complexes showed week promising antifungal activities [21]. figure (2)

Conclusion

The complexes are obtained as colored powdered and are characterized using Ft. IR and UV.Vis spectra. The complexes are completely soluble in DMSO.

Effects of compounds on	[Cr(CUM)(Phe) ₂]Cl	[Fe(CUM)(Phe) ₂]Cl

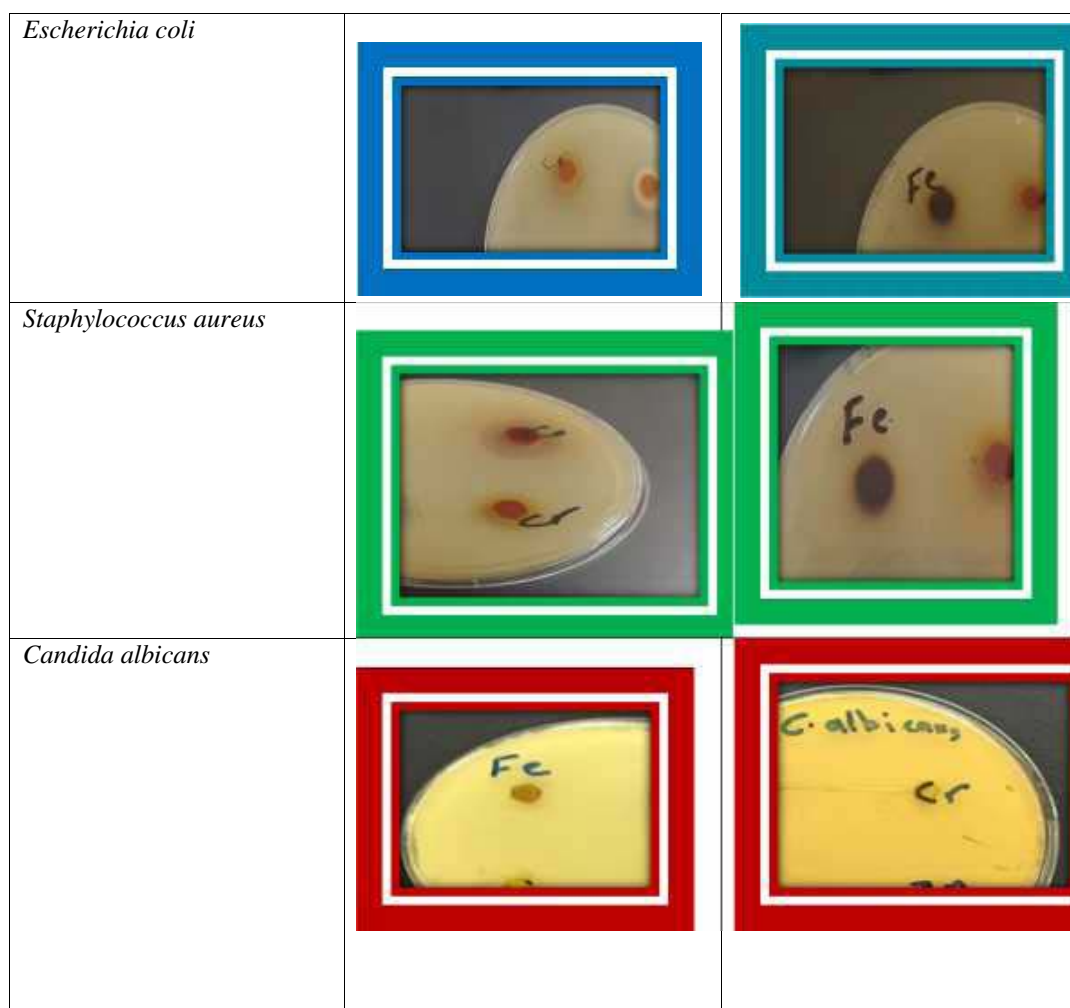


Figure (2). Shows The biological activities

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